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Synthesis and Evaluation of C_2-symmetric Bis-Sulfinamides as Effective Ligands in Rhodium Catalyzed Addition of Arylboronic Acids to Cycloalkenones[#]

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Abstract: Synthesis of novel C_2-symmetric 1,2- 1,3- and 1,4- bis-sulfinamides and their use as effective ligands in rhodium (I) catalyzed asymmetric conjugate addition of arylboronic acids to cyclohexenone and cyclopentenones is described. C_2-symmetry as well as chirality at the sulphur center in the ligand is crucial for the high enentioselectivity in the 1,4-addition reaction. It was also observed that the conjugate addition proceeded with good selectivity with Wilkinson's catalyst as the rhodium source.

Keywords: Conjugate addition, Chiral sulfinamides, C_2-symmetry, Asymmetric catalysis

Introduction

The discovery of chiral diene/ phosphine rhodium complexes catalyze the enantioselective conjugate addition of arylboronic acid to cyclohexenones by Hayashi and Miyura led to a virtual explosion in the development of a number of chiral diene/ phosphine rhodium complexes for this useful transformation.[1] A plethora of publications describing the synthesis and screening of a variety of chiral diene/ phosphine ligands in combination with the rhodium catalysts were reported in literature.[2] Recently, ligands containing chiral sulphur-olefin moieties are shown to exert excellent enantioselectivity in the asymmetric conjugate addition of arylboronic acids to cycloalkenones.[3] A series of structurally diverse sulfoxides and sulfinamides embodied with an olefin moiety were proved to be good ligands in the conjugate addition of arylboronic acids to cycloalkenones (Fig-1) owing to their ease of preparation, stability and affinity to bind to metal center. Although, a number of chiral sulfinamides comprising an alkene tether were tested for their efficiency in the conjugate addition reactions, the efficiency of C_2-symmetric sulfinamides was not examined. Herein, we report the synthesis and evaluation of C_2-symmetric 1,2, 1,3 and 1,4 bis-sulfinamides **1-4** possessing a homoallyl tether as liagnds in rhodium catalyzed conjugate addition of aryl boronic acids to unsaturated cyclic ketones. The sulfinamides with homoallyl tether were chosen as the ligands as they are easy to synthesize from the established allylation of sulfinimines[4] with excellent diastereoselectivity and would exert similar properties to the sulfur based olefin ligands reported for rhodium catalyzed conjugate addition reactions.

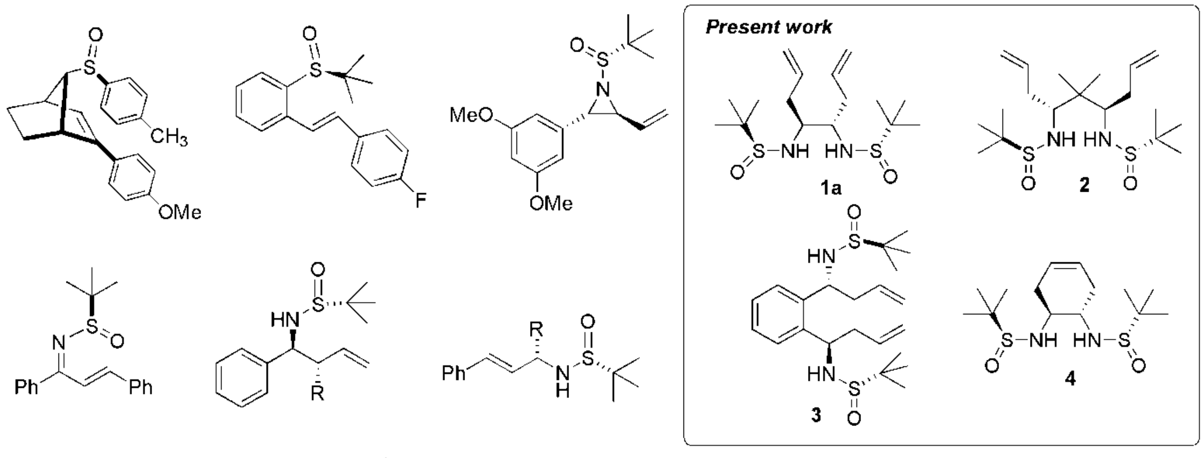

Fig-1: Representative chiral sulfur-alkene ligands in Rh-catalyzed asymmetric conjugate addition of arylboronic acids